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MECHANISTIC ASPECTS OF REACTIONS INVOLVING Ag(II) AS AN OXIDANT

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CONTENTS

A. INTRODUCTION

The 1962 review by McMillan [1] on the higher oxidation states of silver devotes only a small section to kinetic and mechanistic aspects of the reactions of silver(II) compounds. Since then, in parallel with the generally increased interest in mechanistic aspects of inorganic reactions, a great deal of work has been published on the reactions of Ag(II) as an oxidant. The main purpose of the present review is to summarise and assess this more recent work.

Interest in the chemistry of Ag(II) was stimulated nearly fifty years ago in

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a series of papers by Noyes et al. [2–6] on argentic salts in acid solution (the term "argentic" was used to describe both Ag(II) and Ag(III) compounds) notable for the quality of the experimental work (and for an expansive style of writing that would not be permitted by most modern editors!). A recurring theme in this series of papers is a discussion of the extent and importance of the disproportionation of Ag(II) to give Ag(I) and Ag(III). This question and others concerning the nature of Ag(II) solutions are of relevance to more recent work on oxidations by Ag(II) compounds. We therefore begin with a brief account of the preparation and properties of Ag(II) solutions as used in the mechanistic studies that form the main basis for this review. The disproportionation of Ag(II) is also of importance in discussions of the function of Ag(I) as a catalyst for various oxidation–reduction reactions (see, for example, McMillan [1] and House [7]).

B. SILVER(II) IN AQUEOUS SOLUTION

(i) Methods of preparation

Noyes et al. [2] have given an account of early attempts to prepare "argentic" solutions. These include dissolution in nitric acid of the black deposits obtained at the anode during the electrolysis of neutral silver nitrate solutions, and the oxidation of Ag(I) compounds by $S_2O_8^{2-}$, O_3, PbO_2, BiO_2 or F_2. The preparation from silver(I) nitrate and ozone is described in detail by Noyes et al. [2] but subsequently this method has only rarely been used [8]. The most popular methods in recent times have been either to dissolve AgO in the appropriate acid medium (the AgO is obtained commercially or by the oxidation of $AgNO_3$ with $K_2S_2O_8$ [9]) or by anodic oxidation of Ag(I) solutions.

Davis and Lingane [10] have described the latter method. In most cases reference has been made directly or indirectly to the procedures given by Noyes et al. [4,6] and by Veith et al. [11], but a few authors [12–14] have given a little more information about the particular electrolytic methods employed. Oxidation of Ag(I) compounds by peroxodisulphate [15–17] and pulse radiolysis [18–21] have also been used as sources of Ag(II). Heterocyclic and macrocyclic amine complexes of Ag(II) and Ag(III) have been reviewed by Po [22].

(ii) Spectra

(a) Perchloric acid solutions

Spectra of solutions of Ag(II) perchlorate (prepared from $Ag(I)ClO_4$ and ozone) in the range 350–750 nm have been reported by Kirwin et al. [8].

These spectra show a maximum at 475 nm ($\epsilon_{475} = 140 \pm 7$ M^{-1} cm^{-1}) and a shoulder at 575 nm. No significant change in ϵ_{475} was found in solutions containing from 1.5–6.0 M $HClO_4$, but changes were observed near 575 nm and 380 nm. Huchital et al. [23] give ϵ_{max} (470 nm) = 140 M^{-1} cm^{-1} and they found that the spectrum of Ag(II) in 4 M $HClO_4$ agrees with that reported by Kirwin et al. [8] for 3 M $HClO_4$. But no changes in the shape of the band in the 540–560 nm region or in the band at 380 nm were observed at higher acidity. The maximum at 475 nm was confirmed by Rechnitz and Zamochnick [24] (who obtained their solutions from AgO and $HClO_4$) but they found an additional maximum at 275 nm with variable absorbance over a range of $HClO_4$ concentrations from 6.0 to 11.5 M. No isosbestic points were observed. Veith et al. [11] using solutions obtained by anodic oxidation of $Ag(I)ClO_4$, found $\lambda_{max} = 470$ nm in 3.0 M $HClO_4$, and Honig and Kustin [25] obtained the value $\epsilon_{470} = 138 \pm 2$ M^{-1} cm^{-1} in 1.5–6.0 M $HClO_4$ and $\mu = 5.60$ M. This value was essentially confirmed by Indrayan et al. [17] who give a rather confused account of earlier reports and interpret their spectroscopic measurements as evidence for the formation of $AgClO_4^+$ and $Ag(ClO_4)_2$.

Thus, there seems to be fairly general agreement about the values of λ_{max} (470–475 nm) and ϵ_{max} (ca. 140 M^{-1} cm^{-1}) but some disagreement regarding other regions of the spectrum. Several authors [13,14,26–28] have used the above results in kinetic studies.

(b) Nitric acid solutions

McMillan and Smaller [29] have reported the spectrum of Ag(II) in 1 : 4 HNO_3 (ca. 3 M) in the region 350–600 nm. A maximum occurs at 390 nm but no extinction coefficients were given. A more detailed study was made by Kirwin et al. [8], who found, in the region 350–750 nm, both λ_{max} (380–400 nm) and ϵ_{max} shifting with nitric acid concentration ($\epsilon_{max} \sim 950$ M^{-1} cm^{-1} in 1.5 M HNO_3 and ϵ_{max} 2300 M^{-1} cm^{-1} in 6.0 M HNO_3). These results were generally confirmed by Honig and Kustin [25] who found the peak in the spectrum shifted from 370–390 nm as the nitrate ion concentration increased from 0.78 to 6.25 M (only a shoulder was observed below 0.5 M nitrate). Other ϵ values (M^{-1} cm^{-1}) reported are: $\epsilon_{394} = 2530 \pm 50$ (4.66 – 6.18 M HNO_3) and $\epsilon_{394} = 3400$ (8.82 M HNO_3) [30]; $\epsilon_{390} = 2860 \pm 50$ (6.17 M HNO_3) [31]; $\epsilon_{365} = 2086 \pm 39$ and $\epsilon_{685} = 269 \pm 4$ (both at 6.11 M HNO_3) [32]. Again, in comparable situations, there seems to be general agreement among different workers.

(c) Other solutions

A spectrophotometric study of Ag(II) in H_2SO_4 (0.25–18 M) [12] showed the presence of one peak (or shoulder) near 360 nm and another near 260 nm, each with absorbance varying with acid concentration. For the solutions in 12 and 18 M H_2SO_4 an isosbestic point was observed at 310 nm. Values of ϵ were not calculated (except $\epsilon_{361} = 3.11 \times 10^4$ M^{-1} cm^{-1}) but can be obtained from the absorbance values given.

Similar measurements on solutions in phosphoric acid [33] appear to be much less reliable, partly as a result of decomposition of Ag(II) and partly because extinction coefficients at ca. 500 nm are small. (Reported absorbance values at this wavelength are in the range 0.031–0.067, leading to ϵ values of about 20 M^{-1} cm^{-1}. No reproducible isosbestic points were observed.)

Pulse radiolysis of Ag(I) solutions gives solutions containing the species Ag^{2+}(aq), $Ag(OH)^+$ and $Ag(OH)_2$. The spectra of these species are reported by Asmus et al. [21] and show the following features:

	λ (nm)	$\epsilon 10^3$ (M^{-1} cm^{-1})	
Ag^{2+}	275	5.4 ± 0.05	(cf. ref. 24)
$Ag(OH)^+$	315	5.5 ± 0.05	
$Ag(OH)_2$	290	6.5 ± 0.05	

Small shoulders at 400–500 nm were observed for $Ag(OH)^+$ and $Ag(OH)_2$.

A detailed investigation into the spectra (350–650 nm) of $Ag(bipy)_2^{2+}$ in aqueous nitric acid demonstrates the effects of $Hbipy^+$ concentration [34] (this paper also provides a brief review of earlier work on the electronic spectra of $Ag(bipy)_2^{2+}$ solutions).

C. EQUILIBRIA IN Ag(II) SOLUTIONS

In most of the mechanistic studies reviewed here the Ag(II) oxidant has been used in the form of an aqueous acidic solution. These solutions are strong oxidising agents (Table 1) and, in addition to products formed from the oxidation of water, they may contain various species arising from processes such as complex formation with the anions of the acid, disproportionation and hydrolysis. From their spectroscopic investigations (see above) Rechnitz and Zamochnick [24] have concluded that Ag(II) is appreciably complexed by perchlorate and that at least three different Ag(II) species are involved. However, this conclusion has been questioned [25] and Noyes et al. [6] found no evidence for perchlorate complexes. Rechnitz and Zamochnik have also postulated the existence of two sulphate complexes [12] and two phosphate complexes [33]. The existence of nitrate complexes could account for the differences in *E* values in nitrate and perchlorate media [6], and Honig and Kustin [25] have calculated from spectroscopic data the

TABLE 1

Reduction potentials (E) for the couple Ag(II)/Ag(I)

E (V)	Temp. (°C)	Medium	Ref.
1.914±0.002	0	1–4 M HNO_3	4
1.932	25	4 M HNO_3	6
2.00	25	4.0 M $HClO_4$	6
1.978	−5	6.5 M $HClO_4$	35
1.453 [a]	25	H_2SO_4	36

[a] This value is for a silver(II)–bipy complex but, as the experiments were carried out in the absence of excess of bipy, there seems to be some doubt as to whether it applies to $Ag(bipy)_2^{2+}$ or to $Ag(bipy)^{2+}$ as the Ag(II) complex (see ref. 34).

formation constant (K) for $AgNO_3^+$ (K = ca. 0.94 M at 22.5°C, with ϵ_{390} for $AgNO_3^+ = (3.24 \pm 0.4) \times 10^3\ M^{-1}\ cm^{-1}$).

The hydrolysis of the $Ag^{2+}(aq)$ ion (eqn. (1)) was also studied by Honig and Kustin [25] who concluded that at 22.5°C, $K_h \simeq 0.69$ M.

$$Ag^{2+}(aq) \overset{K_h}{\rightleftarrows} AgOH^+ + H^+ \qquad (1)$$

As these authors point out, and as can be seen from their results (e.g. Fig. 2 of ref. 25), this is a rough estimate. Using another approach they obtained "very rough" values of K_h ranging from 0.15 to 0.63 M. The estimates of K_h are somewhat uncertain because of the complicated nature of the system (in which complexation of Ag(II) with nitrate also occurs—see above) and the need to make some assumptions (e.g. that ϵ_{390} for $Ag^{2+}(aq)$ and $AgOH^+$ are equal). These points are discussed fully and critically in the paper, which repays careful reading. We have drawn particular attention to this aspect of Ag(II) solutions because the value of K_h reported by Honig and Kustin has been used frequently by later workers in attempts to account for the acid dependence of reactions in which Ag(II) is used as oxidant. In a more recent paper Asmus et al. [21] have reported "the pK value of 5.35 for the equilibrium $H^+(aq) + Ag(OH)^+ \leftrightarrows Ag^+ + H_2O$". This is a very surprising result and it is difficult to see how it can be reconciled with the value of K_h given by Honig and Kustin. Asmus et al. have also reported the solution spectra of $Ag^{2+}(aq)$ and $Ag(OH)^+$ which show that, contrary to the assumption of Honig and Kustin, the values of ϵ_{390} for these two species are not equal. It therefore appears that there is an urgent need for a reappraisal of the question of the hydrolysis constant of $Ag^{2+}(aq)$. Further discussion of this controversial issue is given below.

D. REACTIONS OF Ag(II) SOLUTIONS

(i) Oxidation of H_2O

An additional complication accompanying the use of aqueous Ag(II) solutions as oxidants is the fact that these solutions are metastable with respect to oxidation of the solvent, a reaction with the stoichiometry shown in eqn. (2) (ref. 5).

$$4\ \mathrm{Ag(II)} + 2\ \mathrm{H_2O} \rightleftarrows 4\ \mathrm{Ag(I)} + 4\ \mathrm{H^+} + \mathrm{O_2} \tag{2}$$

From the fact that the rate of formation of Ag(II) from Ag(I) and ozone is proportional to $[\mathrm{Ag(I)}]\ [\mathrm{O_3}]$, Noyes et al. [2,3] concluded that Ag(III) is the initial product of this reaction. Although this argument may be faulty, the conclusion may well be correct, and their further conclusion that at equilibrium (in nitric acid solutions at low temperature) the product is mainly in the form of Ag(II) seems soundly based on several independent experiments. Thus, they were led to conclude that Ag(II) is subject to disproportionation

$$2\ \mathrm{Ag(II)} \rightleftarrows \mathrm{Ag(I)} + \mathrm{Ag(III)} \tag{3}$$

and that the position of the equilibrium in (3) is well to the left. Reaction (3) has recently been studied by Kumar and Neta [37].

This disproportionation reaction is included as an integral part of several mechanistic schemes used to account for results of kinetic studies on reaction (2), and also for the Ag(I)–Ag(II) exchange reaction [38]. With regard to the kinetics of reaction (2) it seems to be generally agreed that $-\mathrm{d}[\mathrm{Ag(II)}]/\mathrm{d}t$ is a function of the concentrations of Ag(II), Ag(I) and $\mathrm{H^+}$. However, the precise form of the function and the effects of anions such as nitrate and perchlorate still appear to be matters of controversy. There are brief reports on the reduction of Ag(II) by water in sulphuric acid [12] and phosphoric acid [33] media but in attempting to summarise the situation we consider mainly the results of experiments in perchlorate and nitrate media.

Kirwin et al. [8] found that in perchloric acid at a given acid and perchlorate concentration $-\mathrm{d}[\mathrm{Ag(II)}]/\mathrm{d}t$ is proportional to $[\mathrm{Ag(II)}]^2/[\mathrm{Ag(I)}]$, a result confirmed in a brief statement by Rechnitz and Zamochneck [24]. Some parts of reference [8] are difficult to understand but the authors reach the conclusion that the rate of decomposition of Ag(II) also involves an inverse square dependence on acidity and that a factor $[\mathrm{ClO_4^-}]^2$ may also be involved. No satisfactory explanation for the perchlorate effect could be suggested but the other results are accounted for by the mechanism

$$\left.\begin{aligned} &2\ \mathrm{Ag^{2+}} \overset{K}{\rightleftarrows} \mathrm{Ag^+} + \mathrm{Ag^{3+}} \\ &\mathrm{Ag^{3+}} + \mathrm{H_2O} \overset{K_1}{\rightleftarrows} \mathrm{AgO^+} + 2\ \mathrm{H^+} \end{aligned}\right\}\text{Rapid}$$

$$AgO^+ \xrightarrow{k} Ag^+ + \tfrac{1}{2}O_2 \text{ (Rate determining)} \tag{4}$$

which leads to the expression

$$-\mathrm{d}[Ag(II)]/\mathrm{d}t = \frac{kKK_1[Ag^{2+}]}{[Ag^+][H^+]^2} \tag{5}$$

This scheme is supported by further experiments [39] in which Ag(II) is generated from the rapid reaction

$$Co(III) + Ag(I) \rightleftarrows Co(II) + Ag(II) \tag{6}$$

The observed rate of reduction of Ag(II) by water is then governed by this equilibrium and the rate constants can be related to variations in the concentrations of Co(III), Ag(I) and Co(II). However, Wells [40] has pointed out that the results reported by Kirwin et al. [8] can be explained on the basis of an alternative mechanism involving Ag(II) dimers instead of invoking the participation of Ag(III) via the disproportionation reaction (3). Wells [40] has also criticised the treatment by Kirwin et al. [8] of their results on the acid dependence in these reactions and he concludes that the acid dependence found by them is better represented by replacing the term $[H^+]^2$ in eqn. (5) with the term $([H^+]^2 + K_h[H^+])$, where K_h refers to eqn. (1). It is not entirely clear which results of Kirwin et al. have been used by Wells in his re-calculations but if, as seems likely, his assessment is based on a comparison of his Fig. 1 with Fig. 7A of ref. 8 then there seems little to choose between the two interpretations. If, as seems possible, the value of K_h is small enough to make $K_h[H^+] \ll [H^+]$ in these experiments then the two interpretations would be practically equivalent.

The reduction of Ag(II) by water in aqueous nitric acid is rather more complicated. Noyes et al. [5] found a two-term rate law in which, in addition to a term similar to that in eqn. (5), the Ag(II) concentration appeared to the fourth power. Po et al. [31] carried out an extensive study of the reaction and have shown that it is second order in [Ag(II)] when $[Ag(II)] > 1 \times 10^{-4}$ M, but first order in [Ag(II)] below this concentration. In the two concentration ranges the data are satisfied by different complex rate-equations, each involving both Ag(I) and acid concentrations. Two separate mechanistic schemes are proposed, one for the second-order process, involving steady-state concentrations of Ag(III), AgO^+, H_2O_2 and O_2H, and another for the first-order process, involving $AgONO_3^-$, OH, NO_3, H_2O_2 and OH_2 (i.e. no Ag(III) species). The acid dependences in the two schemes are considered to arise from reactions (7) and (8)

$$Ag(III) + H_2O \rightleftarrows AgO^+ + 2\,H^+ \tag{7}$$

$$AgNO_3^+ + H_2O \rightleftarrows AgONO_3^- + 2\,H^+ \tag{8}$$

In summary, it appears that the reduction of Ag(II) by water is a very complicated process and that no concise account can be given of any generally accepted mechanism for it. Fortunately the reaction can be effectively suppressed in the presence of high Ag(I) and H^+ concentrations and so it does not normally interfere in the study of the reduction of Ag(II) by other substrates.

(ii) Reactions of Ag(II) with H_2O_2

Hydrogen peroxide appears as an intermediate in several postulated mechanisms for the reduction of Ag(II) by H_2O [2,31]. Po et al. [31] state that Noyes et al. [1] observed the reaction of Ag(II) with H_2O_2 to be rapid, but actually this was an assumption not an observation. That the reaction of $Ag^{2+}(aq)$ with H_2O_2 is in fact rapid was demonstrated by Wells and Mays [41] who found that the rate was independent of $[Ag(II)]/[H_2O_2]$, [Ag(I)] and acidity, having a rate law similar to that for the reaction of Mn^{3+} with H_2O_2. Two studies have also been published on the kinetics of the reaction between H_2O_2 and $[Ag(bipy)_2]^{2+}$ [42,43]. In each case the reaction was found to be first-order in [Ag(II)] and in $[H_2O_2]$, leading to a mechanism in which the rate-determining step is the formation of HO_2 from a silver(II) complex, followed by rapid oxidation of HO_2 to H^+ and O_2. The two studies differ in their findings on the acid dependence of the reaction rate but these differences can be attributed to differences in the experimental conditions. The experiments of Heyward and Wells [43] were carried out in the acidity range 0.1–1.0 M and in the presence of an excess of bipy. Under these conditions the reaction is dominated by the equilibrium (9) (which was also the subject of a separate spectroscopic study [34] (see above)).

$$[Ag(bipy)_2]^{2+} + H^+ \overset{K_h'}{\rightleftarrows} [Ag(bipy)]^{2+} + Hbipy^+ \qquad (9)$$

The kinetic results show that $[Ag(bipy)]^{2+}$ is very much more reactive than the bis-complex so that the important rate-determining step is

$$[Ag(bipy)]^{2+} + H_2O_2 \rightarrow Ag(I) + HO_2 + Hbipy^+ \qquad (10)$$

Po and Chen [42] used much lower acidities and did not add an excess of bipy to their reaction mixtures. Under these conditions the acid dependence is more complicated than that found by Heyward and Wells and can be attributed to rate-determining steps involving the species $[Ag(bipy)_2]^{2+}$ and the more reactive $[Ag(Hbipy)_2]^{4+}$.

(iii) Oxidation of metal ions

In their first paper of the series on argentic salts in acid solution Noyes et al. [2] summarised the results of qualitative experiments on the reduction of silver(II) by various reagents, including several metal ions. Brief kinetic studies were carried out by Lloyd and Pickering [44] (on the oxidation of Mn(II) and Co(III)) who identified the factors affecting the rates of reaction in the course of an investigation into the analytical possibilities of these reactions. Second-order rate constants for the oxidation of Fe(II) by $[Ag(phen)_2]^{2+}$ and by $[Ag(bipy)_2]^{2+}$ are given by Gordon et al. [45] as 1.7×10^6 M^{-1} s^{-1} and 1.4×10^6 M^{-1} s^{-1}, respectively, in 0.5 M H_2SO_4 at 25°C. The oxidation of Tl(I) by Ag(II) in aqueous nitric acid is a reaction with a complex rate-law [30] and the authors have encountered some difficulty in arriving at a satisfactory mechanistic explanation. The reaction was acid-dependent in the range 4.66–8.82 M HNO_3. The behaviour of other metal ions investigated appears to be more straightforward, generally giving rate laws of the type

$$-d[Ag(II)]/dt = k_{II}[Ag(II)][M^{n+}] \tag{11}$$

(k_{II} is the observed second-order rate constant) and, when comparable, there is generally good agreement on the values of rate constants reported (Table 2). The reaction of Ag(II) with Co(II) has also been investigated indirectly by making use of the results of experiments on the catalytic action of Ag(I) in the oxidation of Fe(II) [23] and Cr(III) [46,47] by Co(III). These reactions are considered to involve the process (12) and subsequent oxidation of Fe(II)

TABLE 2

Second order rate constants (k_{II}) for the oxidation of metal ions by Ag(II) in aqueous acidic solutions

Reductant	k_{II} (M^{-1} s^{-1})	Ref. [a]
Fe(II)	1.4×10^5	48
	4×10^5	23
V(IV)	3.8×10^3	48
	4.9×10^3	49
	5×10^3	23
Co(II)	2.4×10^3	48
	1.8×10^3	23
Mn(II)	2.9×10^4	48 [b]
	3×10^4	23
Ce(III)	1.4×10^3	48 [b]
	5×10^3	23 [c]

[a] Experimental conditions: ref. 48, 1–4 M $HClO_4$, $\mu = 4.0$ M, 25°C; ref. 23, 4 M $HClO_4$, excess Ag(I), 25°C; ref. 49, 0.99–5.79 M $HClO_4$, $\mu = 5.9$ M, 23°C. [b] Value at 4 M $HClO_4$, 25°C. [c] Calculated (see ref. 23) from results of Higginson et al., Discuss. Faraday Soc., 29 (1960) 49.

or Co(III) by the Ag(II) formed.

$$\mathrm{Co(III)} + \mathrm{Ag(I)} \underset{k_{-1}}{\overset{k}{\rightleftarrows}} \mathrm{Co(II)} + \mathrm{Ag(II)} \tag{12}$$

From the kinetic data, values of k (in good agreement from the two reactions studied) can be deduced. Combining these with values of k_{-1} obtained by direct measurement [23] yields values of the equilibrium constant for reaction (12) which agree with values deduced independently [23,24] from the reduction potentials of the couples Ag(II)/Ag(I) and Co(III)/Co(II).

An important feature of the reactions of Ag(II) with metal ions is the fact that in several cases (Fe(II), V(IV) and Co(II)) the rates were found to be independent of acid concentration, at least in the range above about 1.0 M [48]. The reactions of Mn(II) and Ce(III), however, show acid dependence, and the same is true of many other oxidation reactions involving Ag(II) (see below). The origin of the acid dependence (or its absence) in these reactions has been the subject of some controversy in the discussion of various possible mechanistic schemes. It may therefore be appropriate to discuss this question in fairly general terms before dealing with reactions involving reductants other than metal ions.

(iv) Acid dependence in Ag(II) oxidations

Rate equations deduced from mechanistic schemes generally contain terms in $[H^+]$ because most schemes include reactions that involve rapid proton exchanges. Reference has already been made to the hydrolysis of Ag(II)

$$\mathrm{Ag^{2+}} \overset{K_h}{\rightleftarrows} \mathrm{AgOH^+} + \mathrm{H^+} \tag{13}$$

Other possible reactions are deprotonation (14) or protonation (15) of the reductant, represented in general here as RH.

$$\mathrm{RH} \overset{K_a}{\rightleftarrows} \mathrm{R^-} + \mathrm{H^+} \tag{14}$$

$$\mathrm{RH} + \mathrm{H^+} \rightleftarrows \mathrm{RH_2^+} \tag{15}$$

Rate-determining steps in the mechanism are then generally chosen from reactions (16)–(21), in each of which either $\mathrm{Ag^{2+}}$ or $\mathrm{AgOH^+}$ oxidises one form of the substrate (RH, $\mathrm{R^-}$ or $\mathrm{RH_2^+}$) to give the products or some other species that undergoes further oxidation.

$$Ag^{2+} + RH \xrightarrow{k_1} \text{Products} \tag{16}$$

$$AgOH^{+} + RH \xrightarrow{k_2} \text{Products} \tag{17}$$

$$Ag^{2+} + R^{-} \xrightarrow{k_3} \text{Products} \tag{18}$$

$$AgOH^{+} + R^{-} \xrightarrow{k_4} \text{Products} \tag{19}$$

$$Ag^{2+} + RH_2^{+} \xrightarrow{k_5} \text{Products} \tag{20}$$

$$AgOH^{2+} + RH_2^{+} \xrightarrow{k_6} \text{Products} \tag{21}$$

In expressions for $-d[Ag(II)]/dt$ deduced from schemes that include some or all of the reactions of type (13)–(21), various terms in $[H^+]$ appear in the numerator (depending upon which species in the scheme are considered to be reactive enough to be included) and in the denominator (because of the need to take into account the material balance among the species present in reactions (13)–(15)). It is evident that the existence of the material balance in reaction (13) is independent of the relative reactivities of Ag^{2+} and $AgOH^+$ towards any given substrate. Therefore, as all the reactions we are considering here have Ag(II) as a common reagent, all mechanistic schemes that include reaction (13) must contain the term $(1 + K_h[H^+]^{-1})$ in the denominator of the expression deduced for $-d[Ag(II)]/dt$. Before considering the more general case, we refer to the relatively simple circumstances relevant to the oxidation of the metal aqua-ions mentioned above. For these substrates the values of K_a (eqn. (22)) are small ($pK_a > 7$) and in the acid solutions used the concentration of $M(OH)^{(n-1)+}$ can be ignored in comparison with that of $M^{n+}(aq)$ i.e. $K_a/[H^+] < < 1$.

$$M^{n+}(aq) \rightleftarrows M(OH)^{(n-1)+} + H^+ \tag{22}$$

Furthermore, the concentrations of $M(OH)^{(n-1)+}$ ions are so small that, in view of the large values of k_{II} (Table 2), the assumption that they play a significant part in the mechanistic scheme (i.e. reactions (18) and (19) where, for the metal ion reactions, R^- represents $M(OH)^{(n-1)+}$) would lead to impossibly high values of the rate constants k_3 and k_4. Thus, the scheme for these metal ion reactions is limited to reactions (13), (16) and (17) and, in the case where $[RH]_0 > > [Ag(II)]_0$, leads to the expression

$$k_{II} = \frac{k_1 + k_2 K_h [H^+]^{-1}}{1 + K_h [H^+]^{-1}} \tag{23}$$

where

$$k_{\mathrm{II}} = \frac{-\mathrm{d}[\mathrm{Ag(II)}]/\mathrm{d}t}{[\mathrm{Ag(II)}][\mathrm{RH}]_0}$$

Such an expression was deduced, for example by Baumgartner and Honig [49] for the oxidation of V(IV) by Ag(II). The observation that k_{II} is independent of $[\mathrm{H}^+]$ was interpreted by these authors as meaning that, for the V(IV) reactions, $k_1 \sim k_2$ i.e. that Ag^{2+} and AgOH^+ are equally reactive towards V(IV). However, it has recently been found [48] that the reactions of Fe(II) and Co(II) with Ag(II) are also independent of $[\mathrm{H}^+]$. It would appear to be a great coincidence if in each of the three cases Ag^{2+} and AgOH^+ are equally reactive towards the reductant. Mathematically there are two other ways in which eqn. (23) could be reduced to the required form: (i) if $k_{\mathrm{h}}[\mathrm{H}^+]^{-1} >> 1$ and $k_2K_{\mathrm{h}}[\mathrm{H}^+]^{-1} >> k_1$ then $k_{\mathrm{II}} = k_2$; and (ii) if $k_{\mathrm{h}}[\mathrm{H}^+]^{-1} << 1$ and $k_2K_{\mathrm{h}}[\mathrm{H}^+]^{-1} << k_1$ then $k_{\mathrm{II}} = k_1$. The first possibility seems unlikely as $[\mathrm{H}^+]$ can be as high as 4.0 M in these experiments and this would lead to a very large value of K_{h}, which would be difficult to accommodate in many other reaction schemes involving Ag(II) (see below). The second possibility would require a value of K_{h} only slightly smaller than the one that has been widely used by workers in this field and, in view of the uncertainties discussed above in connection with the hydrolysis of Ag(II), seems a reasonable approach to the problem. The other condition imposed by possibility (ii) is that $k_2K_{\mathrm{h}}[\mathrm{H}^+]^{-1} << k_1$. If $K_{\mathrm{h}}[\mathrm{H}^+]^{-1}$ is small enough (e.g. with $K_{\mathrm{h}} \leqslant 0.1$ M) this condition could still be consistent with the expectation (as pointed out by Baumgartner and Honig [49]) that k_2 should be greater than k_1. Indeed, if the term $K_{\mathrm{h}}[\mathrm{H}^+]^{-1}$ is eliminated from the denominator of (23) the resulting equation (24) accounts for the kinetic results in the reactions of Mn(II) and Ce(III) with Ag(II) [48], where k_{II} is shown to be a linear function of $[\mathrm{H}^+]^{-1}$.

$$k_{\mathrm{II}} = k_1 + k_2K_{\mathrm{h}}[\mathrm{H}^+]^{-1} \tag{24}$$

Some values calculated using this relationship are given in Table 3.

We now return to a discussion of the general mechanism outlined in eqns. (13)–(21). Although a substrate may be capable of undergoing both deprotonation and protonation reactions it seems unlikely in any particular case that both reactions will be mechanistically important at the same time. Consequently we can consider two separate mechanistic schemes: (a) reactions (13), (14) and (16)–(19); and (b) reactions (13), (15)–(17), (20) and (21). These lead to the two general expressions (25) and (26), respectively.

$$\frac{k_{\mathrm{II}}}{n} = \frac{\left(k_1 + k_2K_{\mathrm{h}}[\mathrm{H}^+]^{-1}\right) + \left(k_3 + k_4K_{\mathrm{h}}[\mathrm{H}^+]^{-1}\right)K_{\mathrm{a}}[\mathrm{H}^+]^{-1}}{\left(1 + K_{\mathrm{h}}[\mathrm{H}^+]^{-1}\right)\left(1 + K_{\mathrm{a}}[\mathrm{H}^+]^{-1}\right)} \tag{25}$$

TABLE 3

Values of constants derived from eqn. (24) (k_{II} and $[H^+]$ values from ref. 48)

Substrate	k_1 ($M^{-1} s^{-1}$)	k_2K_h (s^{-1})
Fe(II)	1.4×10^5	0
V(IV)	3.8×10^3	0
Co(II)	2.4×10^3	0
Mn(II)	2.5×10^4	6.2×10^4
Ce(III)	7.5×10^2	5×10^3

$$\frac{k_{II}}{n}=\frac{\left(k_1+k_2K_h[H^+]^{-1}\right)+\left(k_5+k_6K_h[H^+]^{-1}\right)K_c[H^+]}{\left(1+K_h[H^+]^{-1}\right)\left(1+K_c[H^+]\right)} \tag{26}$$

where $k_{II}/n = (-d[Ag(II)]/dt)/([Ag(II)][RH]_0)$ (n is an integer, the value of which depends on the stoichiometry of the reaction) and $[RH]_0 >> [Ag(II)]_0$.

If the conclusions with regard to the reactions of metal ions with Ag(II) are accepted, then both eqns. (25) and (26) can be simplified by removal of the term $(1 + K_h[H^+]^{-1})$ in the denominators. We examine the consequences of this in the discussion below *.

(v) Reactions of Ag(II) solutions with inorganic non-metal substrates

The reactions in this category show a rather variable pattern of kinetic behaviour, but this may be due to the fact that precise experimental results have been difficult to obtain. The oxidation of dithionate by Ag(II) in perchloric acid solutions (1.36–3.0 M) in the presence of an excess of Ag(I) yields sulphate [11] and follows a relatively simple kinetic law

$$\frac{-d[Ag(II)]}{dt}=k[H^+][Ag(II)][S_2O_6^{2-}] \tag{27}$$

This form of rate equation corresponds to a mechanism in which rapid protonation of $S_2O_6^{2-}$ is followed by a slow reaction between Ag^{2+} and

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* In discussing this aspect of the subject we have adopted the symbols used in the general scheme outlined above (eqns. (13)–(21), (25) and (26)) in place of the various systems of labelling rate-constants and equilibrium constants used by different authors. Thus the symbol k_{II} is used to represent an observed second-order rate constant (as defined above), k_1 is used to represent the rate constant for a reaction of type (16) etc., irrespective of the particular symbols used by individual authors. In reading the original papers in conjunction with the following discussion some transliteration will be necessary, but this seems preferable to making frequent statements pointing out the equivalence of the various symbols used.

$HS_2O_6^-$. Thus, it corresponds to a simplified form of eqn. (26) in which k_1, k_2 and k_6 are all zero and the terms in the denominator are absent, i.e. it is equivalent to $k_{II} = k_5 K_c[H^+]$, where K_c represents the equilibrium constant for the protonation of $S_2O_6^{2-}$. The ion $HS_2O_6^-$ must be in small concentration (otherwise the rate of reaction would either be independent of $[H^+]$ or a term $(1 + K_c[H^+])$ should appear in the denominator of the rate equation) and must be very much more reactive than $S_2O_6^{2-}$. The results also suggest that $Ag(OH)^+$ is not present in significant concentration (and is also unreactive), thus adding support to the conclusions reached above from the results of studies with metal ion substrates [48]. However, it should be pointed out that the acid dependence found in the dithionate study is not entirely in accord with the simple eqn. (27) as the order in $[H^+]$ was actually found to be 0.84 and this was approximated to unity [11]. This suggests that a more accurate representation of the results might be given by a rate equation that contained terms such as $(1 + K_c[H^+])$ or $(1 + K_h[H^+]^{-1})$ in the denominator. (This suggestion could not be tested easily because the full results are not given in the paper.)

Two studies have been reported on the oxidation of phosphorus oxyacids. In the case of H_3PO_3[50] the rate of disappearance of Ag(II) is given by a two-term expression. One term is zero order in [Ag(II)] and the other contains the factor $[Ag(II)]^2/[Ag(I)]$. The latter is reminiscent of the behaviour found in experiments on the oxidation of water by Ag(II) (see above) and leads to the suggestion that Ag(III) is involved. The acid dependence of the rates is described as "uncertain experimentally" and is not discussed in detail, so no mention is made of reaction (13). The oxidation of H_3PO_2 [54] is first order in [Ag(II)] and in $[H_3PO_2]$ and is retarded by Ag(I) because an unreactive complex, $[AgH_3PO_2]^+$, is formed. Acid dependence was not examined and the active form of Ag(II) is considered to be the perchlorate complex $AgClO_4^+$. Honig et al. [26] have carried out a detailed study of the oxidation of hydroxylamine and *O*-methyl hydroxylamine. At a given acidity the reactions follow simple second-order rate laws, first order in [Ag(II)] and first order in substrate concentration. The dependence of the second-order rate constants on acidity was also measured and the results were explained in terms of a shift in the material balance of reaction (13), while $Ag(OH)^+$ was considered to be considerably more reactive than Ag^{2+}. At the acidities used the substrates are almost entirely in their protonated forms. This treatment, therefore, is equivalent, in the general scheme outlined above, to reducing eqn. (26) to a simplified form by putting k_1 and k_2 equal to zero and $K_c[H^+] \gg 1$. Thus (26) becomes (28) (cf. eqn. (6) in ref. 26).

$$k_{II}([H^+] + K_h) = k_5[H^+] + k_6 K_h \tag{28}$$

Honig et al. [26] then assume that $k_5[\mathrm{H}^+] << k_6 K_\mathrm{h}$ and obtain

$$\frac{1}{k_{\mathrm{II}}} = \frac{[\mathrm{H}^+]}{k_6 K_\mathrm{h}} + \frac{1}{k_6} \tag{29}$$

which satisfies their experimental results in giving linear plots for k_{II}^{-1} vs. $[\mathrm{H}^+]$. However, if instead we proceed from (28) by assuming that $[\mathrm{H}^+] >> K_\mathrm{h}$ the expected relationship is given by

$$k_{\mathrm{II}} = k_5 + k_6 K_\mathrm{h}[\mathrm{H}^+]^{-1} \tag{30}$$

which can be tested by plotting k_{II} vs. $[\mathrm{H}^+]^{-1}$.

We have tried these plots by using the data of Honig et al. [26] (Tables 4 and 5) and find that they give linear relationships quite as convincing as those in Figs. 5 and 6 of ref. 26.

As the precision of some of the data is admitted to be not very high we feel that there is little to choose between the two different interpretations given by eqns. (29) and (30), the latter being consistent with a value of $K_\mathrm{h} \leqslant 0.1$ M.

(vi) Reactions of Ag(II) solutions with organic substrates

(a) Carboxylic acids

Silver(II) compounds react with carboxylic acids to form Ag(I), CO_2 and (except in the case of HCO_2H) a variety of organic products [16,17].

The product composition has also been studied indirectly in the silver(I) —catalysed oxidations by $S_2O_6^{2-}$ [52]. Detailed kinetic studies have been reported on the oxidation of formic acid [27,32] and on the series acetic, propionic, butyric, isobutyric and pivalic acids [53,54]. There is general agreement that the rate-determining steps in the reactions involve formation of free radicals (the nature of which is open to argument) and that these may then react in a variety of ways to give the products. For example, the presence of free radicals in the oxidation of formic acid is shown by the effect of adding acrylamide [32]. Two electrons per molecule are required for the oxidation so the stoichiometry in general is

$$2\ \mathrm{Ag(II)} + \mathrm{RCO_2H} \rightarrow 2\ \mathrm{Ag(I)} + \mathrm{CO_2} + 2\ \mathrm{H}^+ + \mathrm{R(-H)_{ox}} \tag{31}$$

where $\mathrm{R(-H)_{ox}}$ represents the organic oxidation products. In the detailed kinetic studies there is agreement among different workers that, in the presence of an excess of Ag(I), the rate law is of the form

$$-\mathrm{d}[\mathrm{Ag(II)}]/\mathrm{d}t = k_{\mathrm{II}}[\mathrm{Ag(II)}][\mathrm{RCO_2H}] \tag{32}$$

where k_{II} is a second order rate constant calculated from observed first-order constants for experiments in which $[\mathrm{Ag(II)}]_0 << [\mathrm{RCO_2H}]_0$ and in which other factors (such as [H$^+$]) are kept constant. At low concentrations of Ag(I) the rate law for the oxidation of HCO_2H was found [27] to be more complicated than eqn. (32) and included a second term involving the quantity $[Ag(II)]^2/[Ag(I)]$. This can be accounted for by supposing that when the disproportionation reaction (3) is not effectively suppressed, the reactions of Ag(III) become mechanistically important. It has also been observed independently [53,54], that, for the other carboxylic acids studied, an increase in the concentration of Ag(I) has the effect of increasing slightly the rate of oxidation by Ag(II).

Where direct comparison can be made there is substantial agreement on the actual values of the second-order rate constants reported. For example, the results reported by Mehrotra [54] for a series of acids (at 30°C and [$HClO_4$] in the range 1–4 M) agree remarkably well with the corresponding values reported by Mentasti et al. [53]. The two sets of results [27,32] reported for the reactions of HCO_2H are more difficult to compare because different media were used. In the nitrate solutions used by Miller and Morrow [32] the equilibrium

$$Ag^{2+} + NO_3 \overset{K_4}{\rightleftarrows} AgNO_3^+ \qquad (33)$$

has an important influence, with the result that their values of k_{II} (eqn. (32)) depend on the nitrate concentration (as well as on acidity). However, using the data of Miller and Morrow [32] and assuming that the behaviour they observed can be extrapolated to $[NO_3^-] = 0$, the comparison is shown in Table 4. From the results of Miller and Morrow [32] it is also possible to calculate a value of the equilibrium constant for reaction (33) in good agreement with the value given by Honig and Kustin [25] (see above).

Our general conclusion is, therefore, that, with regard to the experimental results, there is substantial agreement among the various published accounts of oxidation of carboxylic acids by Ag(II). There is, however, considerable uncertainty as to how these results should be interpreted. Thus, in the

TABLE 4

Comparison of observed second-order rate constants (k_{II}) for the reactions of Ag(II) with HCO_2H

[H$^+$] (M)	k_{II} ($M^{-1}\,s^{-1}$)	
1.0	48 [a]	138 [b]
2.0	30 [a]	69 [b]
3.0	21 [a]	34.5 [b]
4.0	15.5 [a]	17.2 [b]

[a] Ref. 27, 22°C, $\mu = 4.0$ M. [b] Ref. 32, 25°C, $\mu = 6.3$ M (calculated for $[NO_3^-] = 0$).

oxidation of HCO_2H the fact that k_{II} (at a given NO_3^- concentration) is proportional to $[H^+]$ has been satisfactorily accounted for [32] in terms of reactions (33)–(35)

$$HCO_2H \overset{K_a}{\rightleftarrows} HCO_2^- + H^+ \tag{34}$$

$$Ag^{2+} + HCO_2^- \xrightarrow{k_3} Ag^+ + \text{Radical} \tag{35}$$

As $K_a/[H^+] << 1$, this mechanism leads to the equation

$$\frac{k_{II}}{2} = \frac{k_3K_a}{(1 + K_4[NO_3^-])[H^+]} \tag{36}$$

The fact that this scheme does not include the hydrolysis of Ag^{2+} (eqn. (13)) means that it contains the tacit assumption that $K_h << [H^+]$ (otherwise the term $(1 + K_h[H^+]^{-1})$ should appear in the denominator of the expression for k_{II}). If we make this assumption explicit then a reaction scheme consisting of equilibria (13) and (33) and a rate-determining step (37) would account equally well for the observed acid dependence.

$$Ag(OH)^+ + HCO_2H \xrightarrow{k_2} Ag^+ + \text{Radical} \tag{37}$$

The kinetic results do not allow a choice to be made between these two schemes. It is also possible that under the conditions used by Miller and Morrow [32], the mechanism involves reactions of the nitrate radical as postulated in the oxidation of Tl(I) by Ag(II) [30]. Pelizzetti and Mentasti [27] adopted for their mechanism the reactions (13), (34), (35) and (37). This leads to (38) and thus accounts for the experimental fact that k_{II}^{-1} is a linear function of $[H^+]$.

$$\frac{2}{k_{II}} = \frac{[H^+]}{(k_2K_h + k_3K_a)} + \frac{K_h}{k_2K_h + k_3K_a} \tag{38}$$

But these authors face a similar ambiguity because (38) would still satisfy the experimental results if either k_2 or k_3 were equal to zero. In addition to these ambiguities there is a further difficulty. The two mechanisms that account for the results of Miller and Morrow [32] both involve the assumption that $K_h << [H^+]$, but the mechanisms that account for the results of Pelizzetti and Mentasti [27] involve the assumption that $K_h \not\ll [H^+]$. This situation draws attention once more to the need for a definitive value of K_h.

An examination of the two papers that report kinetic studies on the oxidation of several aliphatic carboxylic acids [53,54] reveals similar problems. Mentasti et al. [53] account for their results on the basis of the reactions postulated in the case of formic acid (eqn. (27)) together with eqn. (39)

$$Ag^{2+} + RCO_2H \rightarrow Ag^{+} + H^{+} + CO_2 + \text{Radical} \tag{39}$$

Thus, they attribute the acid dependence to equilibria (13) and (40)

$$RCO_2H \rightleftarrows RCO_2^{-} + H^{+} \tag{40}$$

Mehrotra [54], however, using values of k_{II} that are in some cases practically identical with those reported by Mentasti et al. [53], prefers equilibrium (41) rather than (40) to account for the acid dependence and does not include reaction (35) in his mechanism

$$RCO_2H + H^{+} \rightleftarrows RCO_2H_2^{+} \tag{41}$$

There seems to be little to choose between the two methods of treating the data. However, as pointed out by Mentasti et al. [53], reactions (35) and (37) are kinetically indistinguishable so the conclusions reached in the two papers are not fundamentally different. It is concluded by both groups that, as with oxidations involving some other metal aqua ions [55], the hydroxo species is more reactive than the aqua ion. Also, in agreement with the results of product composition experiments [52] (but contrary to the report by Anderson and Kochi [51]), it appears that rates vary with the acid structure. Both groups report, but do not satisfactorily explain, the small but significant accelerating effect of Ag(I).

Walling and Camaioni [52] have suggested that the acid dependence in these reactions could be accounted for by the formation of a series of complexes (eqn. (42)), thus eliminating the need to involve reactions (13) and (41).

$$RCO_2H + Ag(II) \rightleftarrows RCO_2H \cdot Ag(II) \rightleftarrows RCO_2^{-} \cdot Ag(II) + H^{+} \tag{42}$$

If these Ag(II) complexes are present in significant concentrations, such a scheme would lead to a rate equation that is not of simple first-order with respect to $[RCO_2H]$, i.e. contrary to the findings in the case of carboxylic acids [53,54]. (The reaction of $Ag(bipy)_2^{2+}$ with isopropyl alcohol, however, does show this kind of departure from first order behaviour in the substrate concentration [56] (see below)).

If the Ag(II) complexes (eqn. (42)) are present in very small concentrations the prediction is that k_{II} should be a linear function of $[H^{+}]^{-1}$. This is a possible (though not the best) way of fitting the data and is in fact also a consequence of other mechanisms in which reactions (13), (40) and (41) are considered to have small equilibrium constants, i.e. mechanisms leading to modified forms of eqns. (25) and (26) in which the denominators are equal to unity.

In the case of the oxidation of iminodiacetic acid (IDA) and *N*-methyliminodiacetic acid (MIDA) by $Ag(aq)^{2+}$ [57] the situation is equally complicated. These substrates (H_2L) exist mainly in the protonated forms (H_3L^+) under the conditions used, but both H_3L^+ and H_2L may be reactive enough to be kinetically important. The reaction of each of these species with Ag^{2+} and with $AgOH^+$ gives a mechanism with four possible pathways for the formation of Ag(I) and a radical and leads to an equation of type (25) with the term $(1 + K_a[H^+]^{-1})$ omitted. Such an equation is not easily tested without making some simplifications. The data are satisfied by assuming $K_h = 0.4$ M (25°C, $\mu = 4.0$ M) and eliminating from the scheme the reaction between Ag^{2+} and H_3L^+. In such a complicated situation it may be that alternative assumptions would give an equally good account of the results and lead to similar conclusions. The oxidation of IDA and MIDA by Ag(II)$^-$ bipy complexes was also studied [57]. The possibilities in these systems of dissociation (or partial dissociation) of bipy adds a new dimension to the complications encountered, especially as the effect of acid on the Ag(II)–bipy complex is a matter of controversy [34].

(b) Alcohols and phenols

The oxidation of alcohols (to aldehydes or ketones) by aqua-silver(II) in perchloric acid has been investigated by Baiocchi and Mentasti [58,59] and by Wells and Fox [13]. As in the case of carboxylic acids the rate law is of the form

$$-\mathrm{d}[\mathrm{Ag(II)}]/\mathrm{d}t = k_{\mathrm{II}}[\mathrm{Ag(II)}][\mathrm{Substrate}] \tag{43}$$

but in several cases [43,58] the observed second-order rate constant (k_{II}) is a function of both acidity and silver(I) concentration. (Ag(I) has generally been added to suppress the interference of the reaction of Ag(II) with the solvent.) Values of k_{II} decrease with increasing [Ag(I)] but the fact that the reactions remain first order with respect to [Ag(II)] seems to preclude the participation of Ag(III). However, an alternative explanation [13], involving the formation of a silver(I)–radical complex which can undergo a back reaction, accounts for the experimental results [13,58]. In some cases [59] the effect of varying the Ag(I) concentration has not been measured.

The cause of the dependence of k_{II} on acidity is a controversial subject. The rate of oxidation of isopropyl alcohol [13] appears to be independent of $[H^+]$ and this has been attributed to a balance between the two reactions (13) and (44)

$$\text{i-PrOH} + H^+ \overset{K_c}{\rightleftarrows} \text{i-PrOH}_2^+ \tag{44}$$

If these two reactions are included in the mechanistic scheme the rate law deduced contains the term $(1 + K_h[H^+]^{-1})(1 + K_c[H^+])$ in the denominator. This factor remains approximately constant for the range of acidities studied (2–4 M) provided the value of K_h is assumed to be rather larger than expected [19] (see above). An alternative to this treatment would, of course, be to assume that both K_h and K_c are small. In either case the observation by Wells and Fox [13] of acid independence leads to the conclusion that $Ag(OH)^+$ is a much less reactive species than Ag^{2+} towards isopropyl alcohol, analogous to the situation found with Mn(III). (In the reactions of the latter, however, Mn(II) does not have the retarding effect corresponding to that observed for Ag(I) on the Ag(II) oxidation.) For the remaining alcohols that have been studied [58,59] (a series that includes isopropyl alcohol) the values of k_{II} are found to be acid dependent. This behaviour is attributed to reaction (13) alone and the appropriate treatment leads to the conclusion that, as in the reactions of Ag(II) with acids and aldehydes, $Ag(OH)^+$ is significantly more reactive than Ag^{2+}. In the treatment of their data Baiocchi and Mentasti [58,59] have used the values of K_h (eqn. (13)) reported by Honig and Kustin [25] but their results could reasonably be accounted for (and the general conclusion retained) if K_h were given rather smaller values. Heyward and Wells [56] have recently reported the kinetics of the reaction of $[Ag(bipy)_2]^{2+}$ with isopropyl alcohol. Here there is significant departure from first-order dependence of the rate on alcohol concentration and this behaviour can be accounted for by the formation in significant concentration of an alcohol–$[Ag(bipy)_2]^{2+}$ complex (cf. ref. 52). Silver(I) has a retarding effect, as in the oxidation of isopropyl alcohol with $Ag^{2+}(aq)$. The effects of low concentrations of Ag(I) can be studied in the solutions of the bipy complex because the interference from side reactions with the solvent is not so important. The rate constants are also acid dependent, in contrast to the reactions of isopropyl alcohol with $Ag(aq)^{2+}$ [13]. Reactions (44) and (9) are included in the mechanistic scheme to account for this but it seems from an examination of the data that a scheme in which (44) is omitted might also be adequate.

The reaction of 4,4′-biphenyl diol with Ag(II) in perchloric acid solutions [60] is too rapid for measurement by the stopped-flow technique (cf. quinol [26]) but the rate of oxidation of the product, 4,4′-biphenoquinone, has been studied briefly [60]. The rate of this reaction (first order in [Ag(II)] and in [substrate]) increases slightly with acid concentration and the authors have had some difficulty reconciling this fact with the K_h values previously reported. Perhaps the best explanation is (as they suggest as a possibility) some acid catalysis, presumably arising from the reactivity of the protonated substrate.

(c) Aldehydes

For reactions of the series: formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde, isobutyraldehyde and pivaldehyde with Ag(II) [28] the pattern of kinetic behaviour (eqn. 43) found for acids and alcohols is repeated. (In the case of the slightly soluble pivaldehyde the reaction was somewhat more complicated because pseudo first-order conditions could not be achieved and because further oxidation of the pivalic acid product also occurred.) Again, this behaviour can be explained on the basis of rate-determining reactions of Ag^{2+} and $AgOH^+$ with the aldehyde molecules (in their keto or enol forms or, in the case of formaldehyde and pivaldehyde, in

TABLE 5

(i) Rate constants (k) for the reactions of Ag(II) species with organic compounds in weak acid solutions at room temperature

Oxidant	pH	Substrate [a]	k ($M^{-1}\,s^{-1}$)	Ref.
Ag^{2+}	4	Anisole	3.8×10^7	61 [b]
		1,2-DMB	6.0×10^7	61
		1,2,3-TMB	2.5×10^7	61
Ag^{2+}	4	CH_3SSCH_3	5.2×10^8	18
		$C_2H_5SSC_2H_5$	3.8×10^8	18
		CH_3SSCH_3	5.6×10^8	18
		$C_2H_5SSC_2H_5$	7.0×10^8	18
Ag^+	ca. 3	2-MBA	6.8×10^8	62 [b]
		2,3-DMBA	6.7×10^8	62
		2,3,4-TMBA	4.7×10^8	62

(ii) Rate constants (k) for intramolecular electron transfer reactions of Ag(II) complexes

Complex [a]	pH	k (s^{-1})	Ref.
Ag(II)–ethylene glycol	4.7	$(2.8\pm0.8)\times10^3$	20
Ag(II)–glycine	4.4	$(5.2\pm0.5)\times10^6$	19 [b]
$Ag(OH)^+$–pivalic acid	4.3	$(1\ \pm0.2)\times10^4$	19
$Ag(OH)^+$–succinate	5.6	$(2\ \pm0.5)\times10^2$	19
Ag(II)–EDTA	11.0	$8\ \pm2$	19
$Ag(NH_3)_4^{2+}$–glycine	11.5	$(3\ \pm0.7)\times10^3$	19
$Ag(NH_3)_4^{2+}$–AIB	11.5	$(5\ \pm1)\times10^3$	19

[a] DMB = dimethoxybenzene; TMB = trimethoxybenzene; MBA = methoxybenzoic acid; DMBA = dimethoxybenzoic acid; TMBA = trimethoxybenzoic acid; EDTA = ethylenediaminetetraacetic acid; AIB = α-aminoisobutyric acid. [b] Other values are also reported. Ref. 18: for substrates 1,3-DMB; 1,4-DMB; 1,2,4-TMB; 1,3,5-TMB. Ref. 62: for substrates 3-MBA; 4-MBA; 3,4-, 2,4-, 2,6- and 3,5-DMBA; 3,4,5-, 2,4,5- and 2,4,6-TMBA. Ref. 19: for complexes $AgOH^+$ with HOAg(II)Gly, AIB and pivalate; Ag(II) with nitrilotriacetate; $Ag(NH_3)_4^{2+}$ with alanine, AIB and aspartate.

the form of hydrates). In the treatment of the data the values of K_h found by Honig and Kustin [25] have been employed, but smaller values of K_h would do equally well without affecting the general conclusions significantly.

(vii) Reactions of Ag(II) in weakly acid solutions

Several studies [18–20,61,62] have been published on the reactions of organic compounds with Ag(II) at low acidities (pH > 4). (Workers in this field have generally adopted the value of K_h reported by Asmus et al. [21] for reaction (13) (see above).) The Ag(II) is formed from the reaction (45) of OH radicals (generated by pulse radiolysis) with Ag(I), and then reacts with the substrate to give Ag(I) and an organic radical.

$$Ag^+ + (OH) \rightarrow Ag^{2+} + OH^- \qquad (45)$$

In some cases [19,20] it is concluded that formation of a silver(II)–substrate complex precedes the electron transfer step and the rates of complexation and of oxidation are reported. The rate constants for the reaction of Ag(II) with ethylene glycol [20], for example, first increase with the glycol concentration and then reach a limiting value. The kinetic experiments are accompanied by product analyses and the results generally support the view of Walling and Camaioni [52] that Ag(III) does not participate in Ag(I)-catalysed oxidation of organic compounds by $S_2O_8^{2-}$. Some of the kinetic results of these studies are summarised in Table 5.

E. INTIMATE MECHANISMS

So far our discussion has been confined to stoichiometric mechanisms, i.e. the problem of identifying the elementary steps by which a given overall reaction occurs. We now consider the question of intimate mechanisms, which involves an analysis of the elementary rate-determining steps that form part of the stoichiometric mechanisms. An analysis of this kind generally includes a comparison of rate constants for a series of "similar" reactions. In the present case such comparisons are available for the reactions of Ag(II) with several metal ions (section D(iii)) and with several series of organic substrates (section D(vi)). However, as we have seen above, the situation is not as clear as this last sentence implies because the assignment of numerical values to rate constants for particular elementary steps depends on the type of stoichiometric mechanism chosen to account for the experimental results. In many cases this is a matter of controversy, arising mainly from the question of how the acid dependence of the experimental second-order rate constants should be interpreted. This question hinges on the value of K_h (reaction (13), and although this is a difficult issue to resolve, it appears from the general discussion above that a plausible interpretation of nearly all the results reported can be given if it is assumed that $K_h \leqslant$ ca. 0.1 M under the conditions used in most experiments. If the value of K_h is taken to be greater than about 0.1 M then the term $(1 + K_h[H^+]^{-1})$ (which must appear in the denominator of expressions derived for k_{II}, c.f. eqns. (25) and (26)) will often differ significantly from unity and this then makes it difficult to give a satisfactory interpretation of some of the experimental results.

(i) Oxidation of metal ions

The experimental work on the reactions of Ag(II) with metal ions (M^{n+}) has been discussed above (section D(iii)). If the mechanisms of these reactions involve reactions (13), (46) and (47) and if $K_h[H^+]^{-1} << 1$, then eqn. (24) is applicable. Values of constants derived from this relationship are given in Table 3.

$$Ag^{2+} + M^{n+} \overset{k_1}{\rightarrow} Ag^+ + M^{(n+1)+} \tag{46}$$

$$AgOH^+ + M^{n+} \overset{k_2}{\rightarrow} Ag^+ + M^{(n+1)+} + OH^- \tag{47}$$

If reaction (46) occurs by an outer-sphere mechanism then, for Fe(II), Co(II), Ce(III) and Mn(II), the values of k_1 (Table 3) can be identified with k_{12} in the Marcus [63] cross relation

$$k_{12} = (k_{11} k_{22} K_{12} f)^{1/2} \tag{48}$$

where k_{11} and k_{22} are the self-exchange rate constants for Ag^{2+} and M^{n+}, respectively, K_{12} is the equilibrium constant for reaction (46) and

$$\log f = (\log K_{12})^2 / \{4 \log(k_{11} k_{22} / Z^2)\}$$

(Z = collision frequency, 10^{11} dm^3 mol^{-1} s^{-1}). As shown by Arselli et al. [48] the values of k_{11} (dm^3 mol^{-1} s^{-1}) calculated from eqn. (48) are not constant, as expected if a simple outer-sphere mechanism is operative, but vary from 10^4 to 10^{-8} thus leading to the conclusion that an inner-sphere mechanism is operative.

The values of $k_2 K_h$ (Table 3) have also been rationalised in terms of an inner-sphere mechanism (involving OH-bridges) for reaction (47) [48].

(ii) Oxidation of organic compounds

We consider here the results of experiments on carboxylic acids, alcohols and aldehydes (cf. section D(vi)). The situation is complicated by lack of agreement on how the acid-dependence of the observed second-order rate constants (k_{II}) should be explained. It should be noted, however, that this difficulty does not arise from disagreement about the actual values of k_{II} but is a consequence of the fact that, within experimental error, the data can be fitted equally well to more than one equation relating k_{II} to $[H^+]$. For example, the values of k_{II} at 30°C for the carboxylic acids [53,54] can be represented by plots of: (a) $k_{II}(1 + K_h[H^+]^{-1})$ vs. $[H^+]^{-1}$; (b) $k_{II}(1 + K_c[H^+])$ vs. $[H^+]^{-1}$; (c) $k_{II}(1 + K_h[H^+]^{-1})(1 + K_c[H^+])$ vs. $[H^+]^{-1}$; and (d) k_{II}^{-1} vs. $[H^+]$; each giving more or less satisfactory linear relationships for some of the acids. These differences in interpretation arise, therefore, essentially from disagreements about values of K_h and K_c (reactions (13) and (15)).

Fortunately these differences are of relatively minor importance when considering trends in values of rate constants for a series of substrates. In

TABLE 6

Rate constants for the reactions of Ag(II) with organic substrates (rate constants refer to reactions (16)–(18))

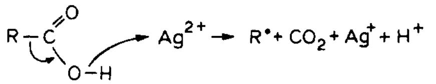
RH	k_1 (M^{-1} s^{-1})	k_2K_h (s^{-1})	$(k_2K_h + k_3K_a)$ (s^{-1})	k_2 (M^{-1} s^{-1})	k_3 (M^{-1} s^{-1})
HCO_2H			35 [c]		3.9×10^5 [d]
CH_3CO_2H	1.9 [a] (5.6) [b]		11.4 [a]	46.8 [b]	
$C_2H_5CO_2H$	7.5 [a] (41.7) [b]		62 [a]	260 [b]	
$CH_3(CH_2)_2COOH$	17 [a] (123) [b]		65 [a]	152 [b]	
$(CH_3)_2CHCO_2H$	40 [a] (836) [b]		1100 [a]	3565 [b]	
$(CH_3)_3CCO_2H$	1000 [a] (8550) [b]		8900 [a]	27900 [b]	
CH_3OH	50 [e]			875 [e]	
CD_3OD	12.5 [e]			165 [e]	
C_2H_5OH	230 [e]			2030 [e]	
C_2D_5OD	50 [e]			530 [e]	
$CH_3(CH_2)_2OH$	300 [e]			2580 [e]	
$(CH_3)_2CHOH$	200 [e] (960) [f]			2580 [e]	
$CH_3(CH_2)_3OH$	325 [e]			5250 [e]	
$(CH_3)_2CHCH_2OH$	500 [e]			14800 [e]	
$CH_3CH_2CH(CH_3)OH$	350 [e]			3900 [e]	
$(CH_3)_3COH$	2.5 [e]			260 [e]	
HCHO	6200 [g]	30000 [g]			
CH_3CHO	300 [g]	5200 [g]			
C_2H_5CHO	1000 [g]	5200 [g]			
$CH_3(CH_2)_2CHO$	1100 [g]	4600 [g]			
$(CH_3)_2CHCHO$	1000 [g]	5200 [g]			
$(CH_3)_3CCHO$	1400 [g]	5000 [g]			

[a] 22°C, $\mu = 4.0$ M (ref. 53), K_h and K_a are equilibrium constants for reactions (13) and (14) respectively. [b] 25°C, $\mu = 4.0$ M (ref. 54). [c] 22°C, $\mu = 4.0$ M (ref. 27). [d] 25°C, $\mu = 4.0$ M (ref. 32). [e] 20°C, $\mu = 4.0$ M (ref. 58). [f] 25.1°C, $\mu = 5.0$ M (calculated from data in ref. 13). [g] 22°C, $\mu = 4.0$ M (ref. 28).

fact, with the qualifications mentioned below, all the results can be discussed on the basis of the same rate-determining steps in each case, viz. reactions (16)–(18). The consequence of the disagreement over values of K_h and K_c is merely that, depending on which values are chosen, the derived constants (k_1, k_2 and k_3) reported by various workers differ by a relatively small factor (< 10). This is shown in Table 6 where some values of k_1, k_2 and k_3 are collected.

There are two further points to make in connection with these results. First, as discussed above (section D(vi)), in some of these reactions there is evidence for the rapid formation of a complex between Ag(II) and the substrate prior to the rate-determining step. Kumar and Neta [19] regard this kind of process as common in the reaction of Ag(II) and they have reported rate constants for complexation in several cases.

This possibility raises further doubts as to how the values of the derived rate constants should be interpreted. In some cases [56] the presence of Ag(II)–substrate complexes can be inferred from the form of the dependence of the rates on substrate concentration. However, if the equilibrium constant for complexation is very small or very large such kinetic evidence would not be available. Where a small extent of complexation occurs this might not be detected by spectroscopic measurements but the interpretation of the derived rate constants should then properly include a factor to allow for this. However, if we ignore this possibility (or assume that the equilibrium constants for complex formation are similar for each substrate) then values of k_1 (Table 6) can be used to identify trends in reactivities of different substrates. For the carboxylic acids [53,54] the electron transfer is easier in the presence of groups that increase electron density at the reaction centre and the rate constants can be correlated with Taft σ^* values. This leads to the suggestion that Ag^{2+} attacks the OH group of the acid.



(49)

For the alcohols [58] and aldehydes [28] the situation is somewhat different because no C–C bond is broken and also because there are other processes to consider (complex formation with Ag(II) in the case of alcohols, and enolisation or hydration in the case of aldehydes), so that the same marked trend with variation of the alkyl group is not observed. These considerations are discussed in more detail in refs. 28 and 58.

The second point, also mentioned previously (section D(vi)), is that reactions (17) and (18) are kinetically indistinguishable so the kinetic measurements do not reveal whether one or the other, or both are involved. This has led to differences of opinion (e.g. Mentasti et al. [53] assume both (17) and (18) occur; Mehrotra [54] assumes only (17); and Miller and Morrow [32] assume only (18)). Also, the rate constant k_2 appears in the derived rate equations as the product k_2K_h and can therefore be evaluated only if the value of K_h is known. (Similarly k_3 appears as the product k_3K_a in equations derived for the reactions of carboxylic acids, but K_a values are generally well known.) Comparison of the values given in Table 6 shows that the trends in the values of $(k_2K_h + k_3K_a)$, k_2 or k_2K_h are similar to the trends in k_1 for each type of substrate. This suggests that reactions (16) and (17) (in both of which the substrate appears as the molecular, i.e. unionised form) should be chosen as the important rate-determining steps in the mechanisms. (This means that the values (Table 6) in the column headed $(k_2K_h + k_3K_a)$ would be better represented as values of k_2K_h.) Mentasti et al. [53] have pointed out that this interpretation would lead to the conclusion that $AgOH^+$ is 10–100 times more reactive than Ag^{2+} towards a given substrate, which is close to other estimates of the relative reactivities of these two species. However, this and the other estimates are based on the assumption that K_h has a value of about 0.2–0.5 M in the temperature range 14–30°C. On this basis it is difficult to reconcile the two values of the constants quoted for formic acid (Table 6). There are also some uncertainties in the comparison of the constants quoted in Table 6 for pivalic acid and those given by Kumar and Neta [19] (cf. Table 5).

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